

# Anisotropic Random Networks of Semiflexible Polymers

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Motivated by the organization of crosslinked cytoskeletal biopolymers, we present a semimicroscopic replica field theory for the formation of anisotropic random networks of semiflexible polymers. The networks are formed by introducing random permanent crosslinks which fix the orientations of the corresponding polymer segments to align with one another. Upon increasing the crosslink density, we obtain a continuous gelation transition from a fluid phase to a gel where a finite fraction of the system gets localized at random positions. For sufficiently stiff polymers, this positional localization is accompanied by a *continuous* isotropic-to-nematic (IN) transition occurring at the same crosslink density. As the polymer stiffness decreases, the IN transition becomes first order, shifts to a higher crosslink density, and is preceded by an orientational glass (statistically isotropic amorphous solid) where the average polymer orientations freeze in random directions.

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*Introduction.* Semiflexible polymers are macromolecules whose behavior is dominated by their bending stiffness. Recent years have seen an explosion of interest in them because some of the most important structural elements of the cytoskeleton (e.g. F-actin) and the extracellular matrix (e.g. collagen) fall in this category [1]. In vivo, these filaments appear in the form of networks or bundles. A first step towards understanding the behavior of such complex aggregates is to study in vitro solutions of many filaments whose interactions are controlled by crosslinkers [2, 3, 4]. There is currently significant activity on the mechanics and elasticity of crosslinked bundles [5, 6]. Previous attempts to theoretically describe the *formation* of ordered structures from disordered solutions use a generalized Onsager approach [7] or a Flory-Huggins theory [8]. In both approaches, the filaments are modeled as rigid rods and the role of thermal bending fluctuations (finite persistence length) is neglected.

In this Letter, we consider randomly crosslinked networks of wormlike chains (WLCs), which are characterized by two parameters: the total contour length,  $L$ , and the persistence length,  $L_p$  [9]. Permanent crosslinks connect randomly chosen pairs of WLCs, such that parallel alignment of the two chains participating in the crosslink is enforced (see Fig. 1). Such crosslinks can be realized experimentally with short actin-bundling proteins such as fimbrin [10]. The parallel alignment acts like an effective Maier-Saupe interaction, giving rise to nematic ordering in the gel with an unexpected strong dependence on the stiffness of the chain. If the persistence length,  $L_p$ , of the WLC is sufficiently large, nematic ordering is observed right at the gel point. The degree of the ordering transition within the gel fraction is discontinuous as in most nematic transitions. However, the orientational ordering is mediated by the crosslinks, so that only the fraction of chains in the gel exhibit nematic ordering.

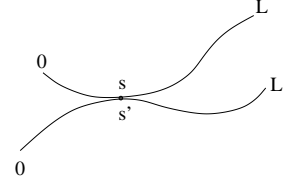


FIG. 1: Crosslinker aligning two wormlike chains at arc length  $s$  and  $s'$ .

Since the gel fraction goes to zero continuously at the gel point, the nematic order parameter is also continuous at the transition. For smaller persistence length, we find a true first order nematic transition inside the gel phase with the distance from the gel point increasing with  $L/L_p$ . Our model also predicts an orientational glass, which is characterized by frozen random orientations of the localised chains in the gel. In this phase the rotational symmetry of the system is broken for any realization of the crosslinks but is statistically restored.

*Model.* We consider a melt of  $N$  identical semiflexible polymers modeled as wormlike chains (WLCs) with contour length  $L$  and persistent length  $L_p$  in three-dimensional space. The Hamiltonian of the system has one part related to the bending stiffness of the WLCs and another part,  $U_{EV}$ , ensuring excluded-volume repulsion [11]:

$$\mathcal{H}(\{\mathbf{r}_i(s)\}) = \sum_{i=1}^N \frac{1}{2} \kappa \int_0^L ds (\partial_s \mathbf{t}_i(s))^2 + U_{EV}.$$

Here  $\kappa = 2L_p k_B T$  denotes the bending stiffness of a WLC and  $\mathbf{t}_i(s) = \partial_s \mathbf{r}_i(s)$  is its tangent vector at arc length  $s$  ( $0 \leq s \leq L$ ) with  $|\mathbf{t}_i(s)| = 1$ . We introduce  $M$  permanent random crosslinks which constrain the system in such a way that they fix the positions of the corresponding segments to overlap *and* their orientations to

be *parallel* or *antiparallel*. The partition function for a specific configuration of crosslinks reads:

$$Z(\mathcal{C}_M) = \left\langle \prod_{e=1}^M \delta(\mathbf{r}_{i_e}(s_e) - \mathbf{r}_{j_e}(s'_e)) \delta(\mathbf{t}_{i_e}(s_e) - m_e \mathbf{t}_{j_e}(s'_e)) \right\rangle,$$

where  $m_e = \pm 1$  and the average,  $\langle \dots \rangle$ , is over all polymer conformations with the Boltzmann weight  $\exp(-\beta \mathcal{H})$ . We treat the constraints imposed by the crosslinks as quenched disorder, and our goal is to calculate the disorder-averaged free energy,  $F = -k_B T [\ln Z]$ , where  $[\dots]$  denotes averaging over all crosslink conformations which are determined by the number of crosslinks,  $M$ , their positions and their polarities,  $\mathcal{C}_M = \{i_e, j_e; s_e, s'_e; m_e\}_{e=1}^M$ . We assume that a disorder configuration with  $M$  crosslinks follows the Deam-Edwards distribution [12]:

$$\mathcal{P}(\mathcal{C}_M) \propto \frac{1}{M!} \left( \frac{\mu^2 V}{N} \right)^M \left\langle \prod_{e=1}^M \delta(\mathbf{r}_{i_e}(s_e) - \mathbf{r}_{j_e}(s'_e)) \right\rangle.$$

The physical content of this distribution is that polymer segments close to each other in the liquid (uncrosslinked) phase, *irrespective* of their relative orientation, have a high probability of getting linked. The parameter  $\mu^2$  can be thought of as a fugacity controlling the mean number of crosslinks per WLC:  $[M]/N$  is of order  $\mu^2$ .

*Order Parameter and Free Energy.* As the number of crosslinks is increased to about one per chain, we expect a gel transition to an amorphous solid state with a finite fraction of WLCs localised at random positions. This spatial localisation due to crosslinking implies for sufficiently stiff chains a restriction also on the orientation of the chains. In a phenomenological ansatz, we model the probability of a single monomer segment,  $s$ , to be found at position  $\mathbf{x}$  with orientation  $\mathbf{u}$  as

$$\langle \delta(\mathbf{x} - \mathbf{r}(s)) \delta(\mathbf{u} - \mathbf{t}(s)) \rangle \propto e^{-\frac{(\mathbf{x} - \mathbf{a})^2}{2\xi^2}} e^{\eta \mathbf{u} \cdot \mathbf{e}}. \quad (1)$$

Here  $\mathbf{a}$  denotes the preferred random position of the monomer,  $\xi$  is the localization length, and  $\mathbf{e}$  is a unit vector with  $\eta$  specifying the degree of orientational ordering. If the nematic aligning interaction induced by the crosslinks is strong enough, then a nematic phase arises. In particular for a (uniaxial) nematic gel  $\pm \mathbf{e}$  is the global axis of orientation. If the aligning interaction is weak, then an orientational glass is expected and  $\mathbf{e}$  is equally likely to point in any direction. For a given number of crosslinks, the effective strength of the nematic interaction is controlled by the persistence length  $L_p$ . For large  $L_p/L \gg 1$ , one crosslink per chain is enough to approximately fix the orientation of the whole chain, whereas for  $L_p/L \ll 1$  many crosslinks are required to achieve nematic ordering. Hence we expect a phase diagram as shown in Fig. (2) with  $\mu^2$  controlling the number of crosslinks and  $L/L_p$  the polymer flexibility. This phase diagram is born out by the calculations, as we now sketch.

In order to calculate the disorder averaged free energy, we apply the standard replica trick,  $[\ln Z] = \lim_{n \rightarrow 0} ([Z^n] - 1)/n$ . We formally decouple individual WLCs from one another by eliminating the single-polymer degrees of freedom in favor of collective fields [13]. In the saddle-point approximation, the density of the system is uniform provided that the excluded-volume interaction is strong enough to prevent it from collapsing due to the crosslinks. Note that this interaction cannot induce an isotropic-nematic transition á la Onsager. The replica free energy per chain then reads:

$$f\{\Omega(\hat{\mathbf{k}}, \hat{\mathbf{u}})\} = \frac{\mu^2 V}{2} \overline{\sum_{\hat{\mathbf{k}}} \int_{\hat{\mathbf{u}}} |\Omega(\hat{\mathbf{k}}, \hat{\mathbf{u}})|^2 - \log z}, \quad (2)$$

where

$$z = \left\langle \exp \left( \mu^2 V \overline{\sum_{\hat{\mathbf{k}}} \int_{\hat{\mathbf{u}}} \Omega(\hat{\mathbf{k}}, \hat{\mathbf{u}})} \right) \frac{1}{2L} \sum_{m=\pm 1} \int_0^L ds e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}(s)} \times \delta(\hat{\mathbf{u}} - m \hat{\mathbf{t}}(s)) \right\rangle_{n+1}^w. \quad (3)$$

Here  $\hat{\mathbf{k}} = (\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n)$ ,  $\hat{\mathbf{u}} = (\mathbf{u}^1, \mathbf{u}^2, \dots, \mathbf{u}^n)$ , and  $\overline{\sum_{\hat{\mathbf{k}}}$  denotes a sum over all wave-vectors except for  $\hat{\mathbf{k}} = (\mathbf{0}, \mathbf{0}, \dots, \mathbf{0})$ . The average is over an  $(n+1)$ -fold replication of the *single* WLC Hamiltonian.

In saddle-point approximation, the field  $\Omega$  satisfies the self-consistent equation:

$$\Omega(\hat{\mathbf{k}}, \hat{\mathbf{u}}) = \sum_{i=1}^N \sum_m \int_0^L \frac{ds}{2LN} \langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_i(s)} \delta(\hat{\mathbf{u}} - m \hat{\mathbf{t}}_i(s)) \rangle, \quad (4)$$

where the average refers to the single chain “partition function” of Eq. (3).  $\Omega(\hat{\mathbf{k}}, \hat{\mathbf{u}})$  acts as an order parameter which distinguishes between various phases, such as liquid, crystalline and amorphous solid with or without orientational order. As discussed above, we focus here on two scenarios for orientational ordering: nematic gels and statistically isotropic amorphous solids (SIAS), where the orientation of the chains is frozen in random directions. Orientational ordering is mediated by the crosslinks, affecting only chains in the same cluster. Chains in *finite* clusters, coexisting with the infinite cluster, move and reorient thermally. Hence only the fraction of localised chains,  $Q$ , i.e. those chains which are part of the *infinite* cluster, exhibit orientational order. Therefore we generalise the order parameter of the isotropic gel to the following form:

$$\Omega(\hat{\mathbf{k}}, \hat{\mathbf{u}}) = (1 - Q) \delta_{\hat{\mathbf{k}}, \hat{\mathbf{0}}} + Q \omega(\hat{\mathbf{k}}, \hat{\mathbf{u}}) \delta_{\mathbf{0}, \sum_{\alpha=0}^n \mathbf{k}^\alpha}. \quad (5)$$

The gel fraction is denoted by  $Q$  and macroscopic translational invariance requires  $\sum_{\alpha=0}^n \mathbf{k}^\alpha = \mathbf{0}$ .

*Statistically Isotropic Amorphous Solid.* In the SIAS the orientation of the WLCs in the gel are frozen, such that the preferred direction fluctuates randomly from chain to chain. Rotational symmetry is broken for any

single realization of disorder but is statistically restored. (This type of order has also been predicted for other systems [15, 16]). The order parameter involves an average over all chains, which is equivalent to an average over all directions. Motivated by the phenomenological picture, we make the following variational ansatz for the order parameter

$$\omega(\hat{\mathbf{k}}, \hat{\mathbf{u}}) = e^{-\xi^2 \hat{\mathbf{k}}^2/2} \int d\mathbf{e} \prod_{\alpha=1}^n e^{\eta \mathbf{e} \cdot \mathbf{u}^\alpha} \left( \frac{\eta}{\sinh(\eta)} \right)^n \quad (6)$$

where the last factor ensures proper normalization of the order parameter,  $\int d\hat{\mathbf{u}} \omega(\hat{\mathbf{k}} = \hat{\mathbf{0}}, \hat{\mathbf{u}}) = 1$ .

Using this ansatz, and taking the limit  $n \rightarrow 0$  followed by  $V \rightarrow \infty$ ,  $N \rightarrow \infty$ ,  $N/V = \text{const.}$ , the free energy per polymer reads:

$$\begin{aligned} f(\xi^2, \eta, Q) = & \frac{(Q\mu)^2}{2} \left( -\frac{3}{2} \ln(\xi^2) - \frac{1}{54} \eta^4 \right) \\ & - \frac{(Q\mu^2)^2}{2} \left( -\frac{3}{2} \ln(\xi^2) - \frac{1}{4} B_1 \frac{1}{\xi^2} - \frac{1}{18} B_2 \eta^4 - \frac{1}{6} B_3 \frac{\eta^2}{\xi^2} \right) \\ & - \frac{(Q\mu^2)^3}{4} \ln(\xi^2), \end{aligned} \quad (7)$$

where we have kept only the leading order terms in  $Q$ ,  $\xi^{-2}$ , and  $\eta$ .  $B_1$ ,  $B_2$ , and  $B_3$  depend on  $l \equiv L/L_p$  through the lowest moments of the WLC conformational probability distribution.

Stationarity of the free energy with respect to  $Q$ ,  $\xi$ , and  $\eta$  yields a continuous gelation transition at  $\mu_c^2 = 1$  characterized by a nonzero gel fraction  $Q \sim 2(\mu^2 - 1)$ , independent of  $l$ . These results are universal for the gelation transition in the saddle point approximation and have been confirmed for various models (e.g. [13, 14, 15]). The localization length and the degree of orientational order depend on the stiffness of the WLC. In the flexible limit, the localisation length is determined by the radius of gyration  $\xi^2 \sim (\mu^2 - 1)LL_p$  and the orientational order goes to zero as  $\eta^2 \sim L_p/L$ . In the stiff rod limit ( $l \rightarrow 0$ )  $\eta^2 \xi^2$  diverges at  $\mu^2 = 1$ . Our perturbative approach breaks down in this singular case where a single increasingly long stiff rod is formed.

*Nematic Gel.* The alignment of the crosslinked polymer segments may trigger an isotropic-to-nematic phase transition, provided a macroscopic cluster of crosslinked polymers exists. For a uniaxial nematic the two directions  $\pm \mathbf{e}$  are equivalent. Hence we sum over these two directions  $\pm \mathbf{e}$  in the phenomenological ansatz (1) and generalize the order parameter to include nematic ordering:

$$\omega(\hat{\mathbf{k}}, \hat{\mathbf{u}}) = e^{-\xi^2 \hat{\mathbf{k}}^2/2} \left( \frac{\eta}{\sinh \eta} \right)^n \prod_{\alpha=1}^n \cosh(\eta \mathbf{u}^\alpha \cdot \mathbf{e}). \quad (8)$$

The experimentally accessible nematic order parameter,

$$\mathcal{S} = \frac{1}{N} \sum_{i=1}^N \frac{1}{2L} \int_0^L ds \langle 3(\mathbf{e} \cdot \mathbf{t}_i(s))^2 - 1 \rangle, \quad (9)$$

is obtained from the generalised order parameter field as

$$\mathcal{S} = \frac{Q\eta}{4} \int_{-1}^{+1} dx \frac{\cosh(\eta x)}{\sinh(\eta)} (3 \cos^2 x - 1), \quad (10)$$

showing clearly that only the gel fraction contributes to the nematic ordering. Even if the nematic transition is of first order - as it will turn out - the jump in the nematic order parameter may be very small due to a small gel fraction and in fact  $\mathcal{S}$  may even be continuous (see below).

If we substitute the above ansatz, Eq. (8), into the saddle-point free energy, we obtain:

$$f(\xi^2, \eta, Q) = f_p(\xi^2, Q) + f_n(\eta, Q) + \mathcal{O}\left(\frac{Q^2 \eta^2}{\xi^4}\right), \quad (11)$$

The positional part of the free energy,  $f_p(\xi^2, Q)$ , is exactly the same as that obtained from Eq. (7) by setting  $\eta = 0$ , whereas the lowest-order in  $Q$  orientational part reads:

$$f_n(\eta, Q) = \frac{(Q\mu)^2}{2} \ln \left\{ \eta \frac{\cosh(\eta) \sinh(\eta) + \eta}{2 \sinh^2(\eta)} \right\} - \frac{(Q\mu^2)^2}{l^2} \int_0^L ds \int_0^s ds' \ln \left\{ \frac{\langle \cosh(\eta \mathbf{e} \cdot \mathbf{t}(s)) \cosh(\eta \mathbf{e} \cdot \mathbf{t}(s')) \rangle_w \eta^2}{\sinh^2(\eta)} \right\}, \quad (12)$$

where  $\langle \dots \rangle_w$  denotes averaging over the WLC conformations. For finite  $\eta$ , stationarity of the free energy with respect to variations in  $Q$  and  $\xi^2$  yields exactly the same results as in the gelation transition considered in the previous paragraph. Since  $\xi^{-2} \sim Q$ , the term which couples

positional and orientational localization is of higher order and can be neglected close to the gelation transition ( $Q \ll 1$ ).

If we expand the nematic part of the free energy up to quartic order in  $\eta^2$ , we obtain the typical Landau free

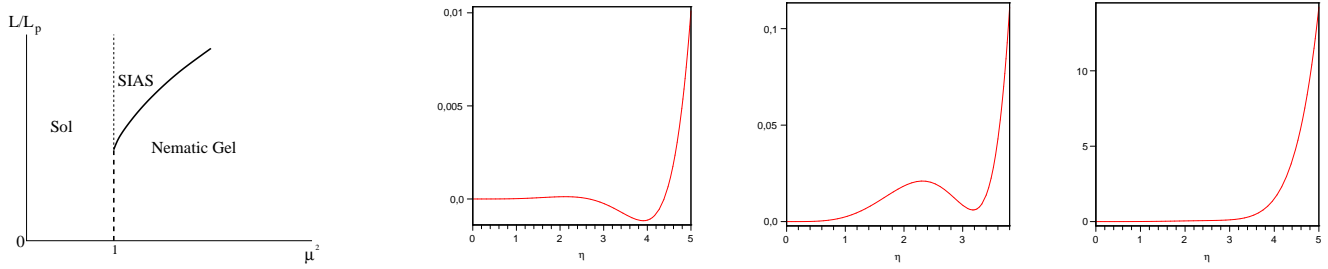


FIG. 2: The first panel shows the schematic phase diagram. The other three panels show the free energy per WLC (in units of  $k_B T$ ) as a function of  $\eta$  for  $l = 0.001$  (second),  $l = 0.15$  (third) and  $l = 0.4$  (fourth) at  $\mu^2 = \mu_c^2 = 1$ .

energy which yields a first order phase transition from an isotropic phase with  $\eta = 0$  to a nematic phase with finite  $\eta$ :

$$\frac{1}{Q^2} f_n(\eta) = a(l, \mu^2) \eta^4 + b(l, \mu^2) \eta^6 + c(l, \mu^2) \eta^8, \quad (13)$$

with  $b(l, \mu^2) < 0$ . The coefficients depend on the control parameters of the system which are the crosslink density (through  $\mu^2$ ) and the single WLC flexibility (through  $L/L_p$ ). The free energy (13) is shown for  $\mu^2 = 1$  and various values of  $l$  in Fig. (2). For stiff chains ( $l = 0.001$ ), the global minimum occurs at finite  $\eta$  already at the gel point, whereas for more flexible chains ( $l = 0.15$ ), the minimum at finite  $\eta$  represents a metastable state with the global minimum at  $\eta = 0$ . In this case, the transition to the nematic happens at a higher crosslink density:  $\mu_*^2 = 1 + \mathcal{O}(l)$ . Finally, rather semiflexible chains ( $l = 0.4$  in Fig. 2) exhibit not even a metastable nematic state at  $\mu^2 = 1$ , but do so at higher crosslink densities: a nematic metastable minimum appears at  $\mu_1^2 > 1$ , which becomes global at the transition point  $\mu_*^2 > \mu_1^2$ . The resulting phase diagram is shown schematically in Fig. (2).

Since the degree of orientational order,  $\eta$ , is finite at the transition, one cannot make quantitative predictions based on the Landau expansion of the free energy. However, we can improve it by expanding  $\langle \dots \rangle_w$  in Eq. (12) in Legendre polynomials. The truncation of the power series expansion becomes less reliable as the WLCs become stiffer. We have checked the behavior of the free energy keeping terms up to  $\eta^{14}$ , and the *qualitative* features of its dependence on the crosslink density are robust. As we increase the crosslink density beyond  $\mu_*^2$ , there is a value at which  $f_n(\eta)$  becomes unstable for large  $\eta$ . At that point, our perturbative approach collapses, since it is based on the assumption of the positional-orientational decoupling close to the gelation transition which is valid for finite  $\eta$ . Also, at the stiff rod limit ( $L/L_p \rightarrow 0$ ),  $f_n(\eta)$  becomes unstable at  $\mu^2 = 1$ .

**Conclusions.** In this Letter, we have shown how the geometry of the crosslinks together with the stiffness of the constituent chains control the orientational order of the random macromolecular network which is formed

upon gelation. Whereas the gel formation is solely controlled by the number of crosslinks, the orientational order induced by localisation is sensitive to both the number of crosslinks and the stiffness of the WLCs. Rather stiff chains tend to exhibit nematic order right at the gel point with a *continuous* isotropic to nematic transition. More flexible chains exist in a phase with frozen random orientation right at the gel point and show a first order nematic transition only at higher crosslink density. Future investigations may extend this work to consider different crosslinking geometries; one important example is polar ordering induced by crosslinks. It would also be of interest to study the possibility of combined nematic and SIAS orderings.

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